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Gas-Phase NMR Studies of *N*,*N*-Dimethylamides. Inter- and Intramolecular Contributions to Internal Rotation Activation Energies

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Temperature-dependent gas-phase ^1H NMR spectra of six C-substituted *N*,*N*-dimethylamides ($XCON(CH_3)_2$) obtained at 500 MHz are consistent with the following free activation energies, $\Delta G^{\ddagger}_{298}$ (kcal/mol): X = Cl, 15.4 (0.2); Br, 14.1 (0.2); N_3, 16.5 (0.1); CN, 19.0 (0.1); CH_2F, 15.2 (0.1); CHF_2, 17.4 (0.1). For all of the amides studied, the observed first-order unimolecular rate constants are consistent with gas-phase $\Delta G^{\ddagger}_{298}$ values for the internal rotation process which are 1–2 kcal/mol lower than reported condensed phase values and, in each case, consistent with a process proceeding via a transition state which has greater steric requirements than the equilibrium conformation.

Introduction

Gas-phase chemical exchange rate constants attributable to the internal rotation process about the peptide bond in amides are faster than corresponding liquid phase rate constants by factors of ca. 25. Our previous studies of gaseous *N*,*N*-dimethylformamide[1] and *N*,*N*-dimethylacetamide[2] yielded free activation energies, $\Delta G^{\ddagger}_{298}$s of 19.4 and 15.3 kcal/mol, respectively. The corresponding values for the neat liquids are 20.9[3] and 18.2 kcal/mol,[4] respectively. Recently, gas-phase free activation energies of several other amides were reported and in all cases faster rate constants and lower activation energies were also observed.[5,6]

Internal rotation in amides has been studied extensively in liquids. Trends in barrier heights of several series of amides which systematically varied the substituent on the carbonyl carbon have been explained on the basis of steric effects and/or substituent electronegativity.[7,8] *N*,*N*-dimethylcarbamyl halides show a trend of increasing barrier height with increasing electronegativity of the halide substituent. In the liquid phase *N*,*N*-dimethylcarbamyl bromide, chloride, and fluoride have $\Delta G^{\ddagger}_{298}$ values for the internal rotation process of 15.7, 16.8, and 18.1 kcal/mol, respectively.[7] In an 18 mol % solution in *sym*-tetrachloroethane, *N*,*N*-dimethylcarbamyl cyanide has $\Delta G^{\ddagger}_{298}$ for its internal rotation process of 21.4 kcal/mol.[7] For *N*,*N*-dimethylcarbamyl azide it is 17.7 kcal/mol. This observation has been explained on the basis of cross conjugation effects. The azide group can stabilize the planar conformation via cross conjugation which diminishes the double bond character of the C–N peptide bond. However, cross conjugation between the azide and carbamyl group is unfavorable and does not occur to an appreciable extent.

Both solvent effects and intramolecular factors can contribute to the observed $\Delta G^{\ddagger}$s in liquids. Comparisons of liquid results with corresponding measurements in the gas phase allow the magnitudes of inter- and intramolecular effects can be elucidated. The present study reports gas-phase free activation energies for internal rotation in *N*,*N*-dimethylcarbamyl chloride, bromide, azide, and cyanide and *N*,*N*-dimethylmonofluoro- and *N*,*N*-dimethyldifluoroacetamide and compares them with previously reported neat liquid and liquid solution results and earlier reported gas-phase values for related molecules.

Experimental Section

N,*N*-Dimethylcarbamyl chloride (DMCC) was obtained from Aldrich Chemical Co. and was used to prepare *N*,*N*-dimethylcarbamyl bromide (DMCB), via exchange with anhydrous HBr, and *N*,*N*-dimethylcarbamyl azide ($DMCN_3$), via exchange with sodium azide, by previously reported methods.[7] *N*,*N*-Dimethylcarbamyl cyanide (DMCCN) was prepared via addition of equimolar amounts of DMCC (Aldrich) and pyridine to a saturated solution of potassium cyanide in acetone which contained a catalytic amount of 18-crown-6 ether under a dry nitrogen atmosphere at 20 °C. The mixture was stirred for 3 days and filtered. DMCCN distilled at 95–97 °C at 10 torr. *N*,*N*-dimethylmonofluoroacetamide (DMMFA) was prepared by dropwise addition of ethyl fluoroacetate to dimethylamine at 9 °C. The reaction mixture was subsequently refluxed for 3 h and the product was vacuum distilled. Dimethyldifluoroacetamide (DMDFA) was prepared by dropwise addition of difluoroacetyl chloride to dimethylamine at 0 °C. All samples were vacuum distilled prior to use and were characterized by their NMR and infrared spectra. The purity of each sample was estimated to be in excess of 98% based on GC analyses using a 6 ft SE-30 column with 5–10-min retention times.

Small differences in limiting ^1H chemical shifts of the methyl resonances of amides have been observed in the liquid phase and are generally even smaller for gases. In order to maximize our data acquisition temperature range, spectra were acquired with a Nicolet 11.8-T spectrometer with ^1H observation at 500 MHz. Additional measurements of DMCC were made with a wide-bore Nicolet 4.8-T spectrometer with proton observation at 200 MHz. All measurements at 500 MHz were made with gas samples contained in 5-mm tubes with vortex plugs which restrict the sample to an 8 cm length within the tube in order to minimize convection. The temperature gradient was 0.2 °C within the active volume region. Temperatures were controlled with a 0.1 °C pyrometer which was calibrated against a copper–constantan thermocouple. Samples were allowed to equilibrate for 10 min prior to spectral acquisition at each temperature. All samples contained approximately 15 μL of the amide which was introduced as a liquid via a syringe; ca. 25 torr of Me_4Si, and 1000 torr SF_6 and were completely vaporized at temperatures where the rate data were obtained. All spectra were acquired in an unlocked mode. The field drift at 500 MHz was typically 4 Hz/h in the unlocked mode and was compensated for electronically. All measurements were made on spinning samples.

Typically, 1200 free induction decays were acquired and stored in 8 K to produce frequency domain spectra with signal/noise ratios of at least ca. 10/1 at 0 °C and between 10/1 and 75/1 at coalescence temperatures. Acquisition times were generally 1.0 s/transient with a 0.1–0.5-s delay and a 74.5° pulse angle (6 μs). In order to characterize the pressure dependence of exchange rate constants in DMCC a series of samples containing 1 torr of DMCC and SF_6 partial pressure ranging from 5 to 500 torr were prepared in 20-mm tubes and their spectra obtained at 200 MHz and 23.3 °C by previously described methods.[5] In all cases, rates were calculated with the iterative line shape analysis program

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TABLE I: Gas- and Liquid-Phase Free Activation Energies for Chemical Exchange and Limiting ^1H Chemical Shift Differences of *N*,*N*-Dimethylamides ($XC(O)N(CH_3)_2$)

	$\Delta G^\ddagger_{298}$, kcal/mol		$\Delta\nu$,[b] ppb	
X	gas[a]	liquid	gas	liquid
H	19.4[c]	20.9 (neat)[d]	<2	166.3[d]
F	17.1 (0.2)[c]	18.1 (0.6) (CCl_4)[f]	25.3[e]	12 neat (16,7% in CCl_4)[f]
Cl	15.4 (0.2)	16.5 (0.5) (CCl_4); 16.8 (0.5) (neat)[g]	196.0	188.3[g]
Br	14.1 (0.2)	15.7 (0.4) (neat)[g]		90[g]
N_3	16.5 (0.1)	17.7 (10% in CCl_4)[f]	69.5	18[g]
CN	19.0 (0.1)	21.4 ($C_2Cl_4H_2$)	243.0	250–266
CH_3	15.7 (0.1)[h]	18.2 (neat)[i]	46.8[g]	180[i]
CH_2F	15.2 (0.1)	16.4 (DMF); 17.0 (ClPh)	136.2	113.1[j]
CHF_2	17.4 (0.1)	18.3 (DMF); 18.8 (ClPh)	180.0	176.0[j]
CF_3	16.4[k]	17.8 (CCl_4)[k]	98.0[k]	123.3[k]
CCl_3	<16	18.3 ($CBrF_2)_2$[j]		114[j]

[a] Samples contained the amide at its vapor pressure and 1000 torr of SF_6; all $\Delta G^\ddagger$ values calculated from NMR rates with $\kappa = 1$. [b] Limiting chemical shift difference of the methylamino ^1H resonances in parts per billion. [c] Reference 1. [d] Reference 3. [e] Reference 6. [f] Reference 14. [g] Reference 7. [h] Reference 2. [i] Reference 4. [j] Reference 8. [k] References 5 and 6.

DNMR5[10] which uses a nonlinear least-squares regression analysis to obtain the best agreement between the observed and simulated spectrum. For each amide, spectra were analyzed as uncoupled A_3X_3 systems. All free induction decays were typically multiplied by exponential line broadening factors of ca. 2 Hz and spectra were zero filled to 16 K. Typically 990 experimental points were used in the analysis of each spectrum, with a digital resolution of 2.05 points/Hz. For each amide the effective line-width parameter, T_2, was obtained at 100–150 °C and was estimated by assuming a linear temperature dependence at each temperature where experimental rate data were obtained. The line width of the gaseous Me_4Si resonance was used to estimate the field inhomogeneity contribution to T_2 at each temperature where rate data were obtained. This factor and the exponential line broadening contributions were added to each interpolated T_2 value.

Limiting chemical shift differences were typically obtained at several temperatures from 0 to ca. 25 °C. Due to low sample volatility useful spectra below 273 K could not be obtained for any of the amides used in this study. Within our uncertainty limits, limiting chemical shifts are not temperature dependent for any of the amides studied. Rates obtained from our exchange broadened spectra have ca. 6% uncertainties ±5–7 deg from coalescence. Since free activation entropies in the gas phase for internal rotation of amides are typically small[1,2] and there are substantial difficulties in rate constant analysis of amides associated with their small limiting chemical shift differences, we did not attempt to obtain a complete set of kinetic parameters characterizing each process. Typically, five rate constants in the coalescence temperature region were determined and used to obtain $\Delta G^\ddagger_{298}$ values.

Results

Comparison of ^1H NMR spectra of gaseous dimethylamides with previous liquid and solution results demonstrates substantial medium effects on conformational exchange rate constants and limting chemical shifts of the dimethylamino resonances. Free activation energies and limiting chemical shifts of gaseous and liquid amides appear in Table I. Specific observations and kinetic data for each molecule are described below.

N,N-Dimethylcarbamyl Chloride. The ^1H methyl resonances (3.00335-ppm downfield from gaseous Me_4Si) of DMCC are separated by 98.09 Hz in an 11.8-T field allowing rate data to be obtained over a temperature range from 303 to 330 K. Coalescence occurred at 314.4 K. Rate data for DMCC appear in Figure 1. Earlier liquid-phase rate constants obtained from spin–echo measurements are plotted for comparison.[11] Gas-phase rate constants are larger than corresponding liquid-phase values by a factor of ca. 9. The gas-phase $\Delta G^\ddagger_{298}$ obtained for internal rotation in DMCC, 15.4 kcal/mol, is 1.4 kcal/mol lower than the value obtained for the neat liquid.[12]

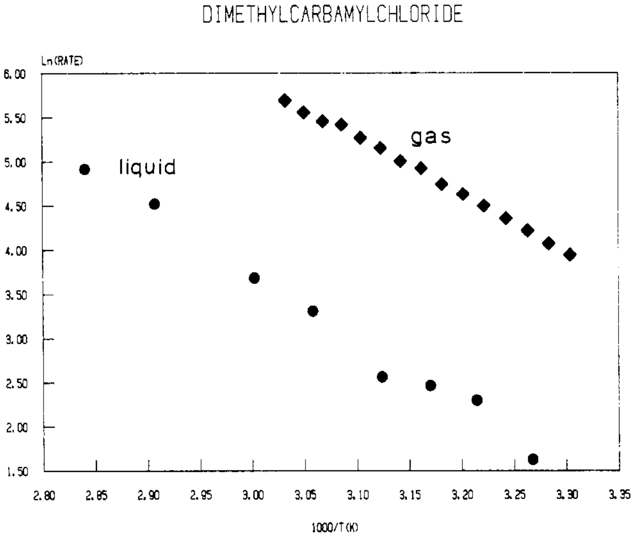

Figure 1. Arrhenius plot of dimethylcarbamyl chloride (DMCC) rate constant data: ◆, gas phase (this study); ●, liquid phase (ref 11).

In order to ensure that the rate constants obtained were first order, and also to determine the falloff behavior of the exchange reaction, pressure dependent studies were also performed. For any gas-phase unimolecular process, the pressure at which the transition between first- and second-order kinetics occurs depends upon the vibrational state density evaluated at the threshold energy.[13] State densities are sparse for rigid molecules at low threshold energies and this results in faster specific rate constants and a corresponding extension of bimolecular kinetics up to higher pressures.[15] Of the amides we have studied, DMCC is most likely to exhibit observable pressure-dependent exchange rate constants based on its relative geometrical simplicity and comparatively low $\Delta G^\ddagger$. In order to obtain information about the pressure dependence of the exchange rate constants, ^1H NMR spectra of a series of eight samples containing 1 torr of DMCC and from 500 to 5 torr of SF_6 in 20-mm tubes were obtained at 296.3 K which is near coalescence at 200 MHz for high-pressure samples. Rate constants obtained for all samples above 23 torr were ca. 30.0 ± 0.3 s^{-1}. At 15 torr the rate constant was 28.0 (0.3) s^{-1}. Reliable

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rate constants below 15 torr could not be obtained due to rapid T_2 relaxation which causes considerable line broadening. Reliable characterization of the bimolecular kinetics associated with chemical exchange was not feasible.

N,N-Dimethylcarbamyl Bromide. Gas-phase NMR spectra of a sample containing DMCB at its vapor pressure and 1000 torr of SF_6 were obtained at 500 MHz. The spectral trace at ambient temperature is a singlet 3.0077-ppm downfield from gaseous Me_4Si and measurements below room temperature allowed determination of the coalescence temperature as 287 K. It was not possible to obtain the limiting chemical shifts of the syn and anti ^1H methyl resonances in order to obtain a precise value of $\Delta G^{\ddagger}$. Table I demonstrates that a simple correlation between gas- and liquid-phase limiting chemical shifts in other amides does not exist, especially for molecules with very small limiting chemical shift differences. If the natural line width in the absence of exchange is significantly less than the line width at coalescence it is generally assumed that this measured line width is equal to $\Delta\nu$, the limiting chemical shift difference in the absence of exchange.[16] This is generally true in liquids. For our amide gas samples where limiting shifts were measured we find that the half-height line width at coalescence slightly exceeds the limiting shift difference. A correlation between the half-height width at coalescence and the limiting chemical shifts was found by comparison of these parameters in several gas-phase amide systems. The half-height width generally ranges from 115 to 120% of the limiting shift separation. A resonable chemical shift difference estimate of ca. 67 Hz for DMCB may be obtained based on analogy and an observed half-height width of ca. 76 Hz at coalescence. (The corresponding observed liquid limiting chemical shift difference is 46 Hz.) With this value, $\Delta G^{\ddagger}$ is 14.1 kcal/mol and a ±5 Hz uncertainty in the limiting chemical shift difference produces an uncertainty range of ±0.2 kcal/mol.

N,N-Dimethylcarbamyl Azide. At room temperature the gas-phase ^1H spectrum of $DMCN_3$ consists of two symmetric resonances separated by 34.77 Hz at 500 MHz centered 2.8605-ppm downfield from gaseous Me_4Si. At temperatures above ca. 300 K spectra show effects of chemical exchange and coalescence occurs at 327.7 K. The rates obtained [T (K), k (s^{-1}): 312.6, 24.1 (4); 326.0, 61.7 (5); 327.7, 68.0 (5); 331.0, 78.9 (6); 340.4, 129.3 (8); 349.7, 225 (1)] are consistent with a $\Delta G^{\ddagger}_{298}$ of 16.5 (0.1) kcal/mol.

N,N-Dimethylcarbamyl Cyanide. The ^1H methyl resonances (3.0050-ppm downfield from gaseous Me_4Si) of DMCCN are separated by 121.4 Hz in an 11.8-T field at 60 °C. Coalescence occurred at 405 K. Five exchange broadened spectra were obtained between 397 and 414 K to yield the following rate constants (T (K), k (s^{-1})): 397.1, 176 (12); 401.3, 210 (10); 405.2, 249 (31); 409.5, 302 (3); 413.1, 363 (3). The corresponding free activation energy, $\Delta G^{\ddagger}_{298}$, is 19.0 kcal/mol. NMR spectra of DMCCN in an 18 mol % solution in *sym*-tetrachloroethane were consistent with a $\Delta G^{\ddagger}_{298}$ of 21.4 kcal/mol.

N,N-Dimethylmonofluoroacetamide. At 273 K the gas-phase ^1H NMR spectrum of DMMFA consists of a well-resolved doublet with a 68.1-Hz splitting centered 2.9670-ppm downfield from gaseous Me_4Si which arises from the dimethylamino protons and a doublet centered 4.786-ppm downfield from gaseous Me_4Si arising from the methylene protons ($^3J_{HF}$ = 48.44 Hz). Coalescence occurred at 312.5 K. Rates obtained from exchange broadened spectra [T (K), k (s^{-1}): 298.3, 40.7 (5); 302.8, 60.0 (5); 307.7, 84.5 (4); 312.5, 137.6 (6); 317.4, 171.5 (8); 322.3, 268.4 (2); 327.2, 340.3 (2)] are consistent with a $\Delta G^{\ddagger}_{298}$ of 15.2 (0.1) kcal/mol.

N,N-Dimethyldifluoroacetamide. At 298 K, gas-phase ^1H NMR spectra of DMDFA show a well-resolved doublet with a splitting of 89.98 Hz centered 3.0000-ppm downfield from gaseous Me_4Si and a triplet ($^3J_{HF}$ = 53.84 Hz) at 5.850 ppm. The doublet coalesced at 357.3 K and rates obtained [T (K), k (s^{-1}): 357.3, 179.0 (4); 359.8, 204.1 (9); 363.8, 249 (2); 369.9, 399 (2)] are consistent with a $\Delta G^{\ddagger}_{298}$ of 17.4 (0.1) kcal/mol.

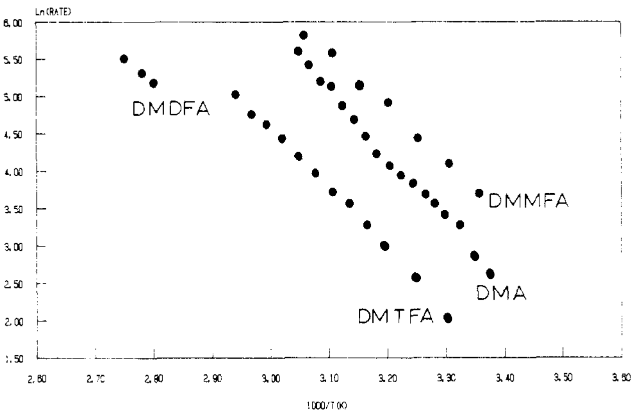

Figure 2. Arrhenius plot of gas-phase exchange rate constant data for substituted acetamides.

Conclusion

Two conclusions follow from the results which are summarized in Table I and shown in Figures 1 and 2. Gas-phase exchange rate constants are significantly faster than corresponding rate constants in liquids. The trend of increasing activation energy for internal rotation with increasing substituent electronegativity is apparent in both phases but is more pronounced for liquid samples. These observations are discussed below.

Gas-phase rate constants of *N,N*-dimethylcarbamyl halides (X = F, Cl, and Br) are inversely related to the electronegativity of the halide substituent. The smaller rate constants and correspondingly higher activation energy of the fluoride correlates with its greater electronegativity and smaller size. The steric model for rotational barriers in amides assumes a decrease in size of substituent will stabilize the ground state and increases the barrier height.[8] A similar trend is observed in the liquid phase[7] for *N,N*-dimethylcarbamyl halides although all the liquid-phase $\Delta G^{\ddagger}$s are ca. 1 kcal/mol higher. The relative gas-phase rate constants and free activation energies of *N,N*-dimethylcarbamyl cyanide and azide also parallel previous liquid-phase results. The gas-phase free activation energy is 2.4 kcal/mol lower for the cyanide and 1 kcal/mol lower for the azide than corresponding liquid-phase values.

Figure 2 shows rate constants obtained for DMMFA and DMDFA as well as previously obtained rate constants for *N,N*-dimethylacetamide (DMA) and *N,N*-dimethyltrifluoroacetamide (DMTFA). The gas-phase free activation energies, $\Delta G^{\ddagger}$ (kcal/mol), are 15.2 (0.1), 15.7 (0.1), 16.4, and 17.4 (0.1) for DMMFA, DMA, DMTFA, and DMDFA. This series has not been studied at similar concentration in the same solvent. For DMA $\Delta G^{\ddagger}$ is 17.3 kcal/mol for chloroform solutions and 18.6 kcal/mol for Me_2SO solutions.[8] For neat DMA liquid, $\Delta G^{\ddagger}$ is 18.1 kcal/mol and for neat DMTFA it is 18.6 kcal/mol. Solutions of DMDFA and DMTFA in DMF have $\Delta G^{\ddagger}$ values of 16.4 and 18.3 kcal/mol, respectively.[8] In the gas-phase the $\Delta G^{\ddagger}$ for DMA is less than for DMTFa and correlates with the greater electronegativity of the CF_3 group. The opposite relation holds for all solution data. It is interesting to note that the barrier heights for the series DMA, DMMFA, DMDFA, and DMTFA do not correlate with either substituent size of substituent electronegativity. In both gaseous and liquid samples, the monofluoro- and difluoroacetamides have the lowest and highest barriers and the acetamide and trifluoroacetamide have intermediate barriers indicating a sensitive balance between several contributing factors.

With no exceptions, gas-phase $\Delta G^{\ddagger}$s for internal rotation about the peptide bond of amides of significantly lower than in liquids. The magnitude of this difference, however, is not uniform and varies from 1 kcal/mol for DMCF to ca. 2 kcal/mol for DMA. $\Delta G^{\ddagger}$ for amide solutions is both solvent and concentration dependent and typically is ca. 0.5 to 1 kcal/mol lower for dilute solutions in nonpolar solvents compared to the neat liquid. However, even dilute solutions of amides in CCl_4 have significantly higher $\Delta G^{\ddagger}$ values than gases. Two types of solvent contributions to $\Delta G^{\ddagger}$ may be considered, dielectric interactions and packing

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forces. The effect of packing forces can be estimated by considering the steric contribution to the free activation volume, $\Delta G^{\ddagger}$, for each process. If we assume that the dimethylamino group rotates and the carbonyl carbon and its substituents remain fixed, all the molecules have similar steric $\Delta V^{\ddagger}$s of ca. 15 cm^3/mol.[2,5] For rotation of the carbonyl moiety against a static dimethylamino fragment, $\Delta V^{\ddagger}$s range from 15 (X = F) to 20 (X = CCl_3) cm^3/mol as a direct function of substituent size. For all the amides studied with the exception of DMF the hard-sphere volume of the carbonyl substituent is larger than the hard-sphere volume of an oxygen atom.[17] Assuming the steric contribution differences of $\Delta V^{\ddagger}$s for all amides studied range from ca. 15 to 20 cm^3/mol, and differences in $\Delta G^{\ddagger}$ for this range, assuming a solvent internal pressure of 4000 atm (CCl_4),[18] may be calculated according to $(\delta(\Delta G^{\ddagger})/\delta P)_T = \Delta V^{\ddagger}$, and range from 0.5 to 2 kcal/mol, one finds that steric packing forces contribute roughly 0.5–2 kcal/mol to the gas–liquid differences in $\Delta G^{\ddagger}$s and can qualitatively account for the variations observed for all of the amides studied.

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Photophysics of Chromium(III) Cyanoammines. Solvent Medium Effects

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Phosphorescence lifetimes, and their temperature dependences, have been determined for $Cr(NH_3)_5(CN)^{2+}$, *trans*- and *cis*-$Cr(NH_3)_4(CN)_2{}^+$ in water, dimethyl sulfoxide, dimethylformamide, and sulfolane solutions, aqueous *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, and $Cr(ND_3)_5(CN)^{2+}$ in D_2O. For the first three species, the τ values at 20 °C are in the 10–100-μs range, i.e., relatively large for Cr(III) acidoammines, and conform to the predictions of previously proposed rules. The rules are also obeyed by other related monocyano complexes. The apparent activation energies for emission vary between 6 and 15 kcal mol^{-1}. For a given complex, the solvent effects on the Arrhenius parameters are considerable, the E^* values changing by as much as 6–7 kcal mol^{-1}. Solvent effects are also observed on the ligand field, quartet absorption bands, as well as on the doublet features, both in absorption and in emission. The results are discussed in terms of the possible processes controlling the doublet-state lifetime in room-temperature solution.

Introduction

Since the recognition that a number of Cr(III) complexes show detectable emission in room-temperature fluid solution,[2] there has been a good deal of study of various facets of the phenomenon. Much of the relevant literature is assembled in ref 3–32. The emission, with few exceptions, is from the lowest lying doublet excited state, ^2E_g in O_h symmetry. The state is a thermally equilibrated or thexi state, and we designate it here as $D_1{}^0$ to avoid symmetry-dependent notations, the superscript zero denoting thermal equilibration.

The radiative lifetime of a $D_1{}^0$ state of Cr(III) is typically in the millisecond range.[33] In room-temperature fluid solution, however, emission lifetimes are usually in the nanosecond to microsecond range and must now be determined by other pro-

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